Applied Surface Science 357 (2015) 333–339

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

The cleavage and surface properties of wet and dry ground spodumene and their flotation behavior

Guangli Zhu, Yuhua Wang*, Xiaowen Liu, Fushun Yu, Dongfang Lu

School of Minerals Processing & Bioengineering, Central South University, Changsha 410083, China

ARTICLE INFO

Article history:
Received 22 April 2015
Received in revised form 16 August 2015
Accepted 30 August 2015
Available online 2 September 2015

Keywords:
Grinding method
Cleavage and fracture
Flotation
Surface broken bonds

ABSTRACT

The flotability of wet and dry ground spodumene was found different when sodium oleate was used as a collector, and the flotation recovery of wet ground spodumene was higher than that of dry ground spodumene. It is well known that the flotability of minerals is closely related with their crystal structures and surface properties, therefore morphology and structure examinations on wet and dry ground spodumene were performed by SEM and XRD. It was confirmed that wet ground spodumene had smoother surface and more exposed {1 1 0} and {1 0 0} planes, while more exposed {0 1 0} planes were found on dry ground spodumene surface. The specific surface areas of wet and dry ground spodumene in size fraction of $-105+38\,\mu m$ were determined to be $0.252\,m^2/g$ and $0.382\,m^2/g$, respectively. However, the maximum adsorption densities of sodium oleate on wet and dry ground spodumene were $21.5\times10^{-6}\,mol/m^2$ and $12.5\times10^{-6}\,mol/m^2$, respectively. The densities of surface Al—O broken bonds were calculated to be 6.376×10^{18}, 4.351×10^{18} and $14.057\times10^{18}/m^2$ for {1 1 0}, {0 1 0} and {1 0 0}, respectively. The result indicated that {1 0 0} and {1 1 0} planes were more favorable for the adsorption of oleic acid ion than {0 1 0} plane.

1. Introduction

Spodumene is a principal economic mineral containing lithium, accounting for more than 90% of world production of Li-bearing minerals. Flotation is the most widely used method for the beneficiation of spodumene. Studies involving spodumene flotation have been carried out by many investigators, most of which are concentrated on the flotability of main minerals in pegmatite spodumene ores and the performance of collectors and depressants [1]. Spodumene belongs to a silicate group called clinopyroxene, one of the single-chain silicates [2]. The greatest challenge of spodumene flotation is the selective separation from other silicate minerals in industry, owing to the close flotability of the main silicate minerals. Considering the similar composition of these silicate minerals, many investigators have studied the principle of crystal chemistry of silicate minerals systematically. Fuerstenau and Raghavan [3] summarized the crystal chemistry of some silicate minerals and explored the correlation of flotability and crystal chemistry, which is a significant reference we can draw from at present. Manser [4] studied the selective flotation of silicate minerals, and made the point that the flotability of silicate minerals was associated with their characteristics of crystal chemistry, especially the ratio of Si to O, the activity of surface ions, and the active regions.

As many beneficiation processes such as flotation are dependent on the surface chemical reactions occurring on the surface of the minerals, it has to be noted that the cleavage and fracture characteristic of minerals during crushing and/or grinding plays a vital role in the subsequent processing. The cleavage and fracture of minerals has a close relationship with their crystal structures since the cleavage and fracture always happens along the direction of the weakest interplanar bond forces. The crystal structures determine the surface properties, such as the polarity, unsaturated bonds and the formation of microstructures. It is of great significance to master the crystal structure of minerals and their principle of cleavage and fracture to predict the cleavage plane of minerals. Moon and Fuerstenau [5] calculated the number of broken bonds and broken ionic bond strength per unit area at four spodumene surfaces, and concluded that the cleavage of spodumene occurred along the weakest {1 1 0} plane, which corresponded to the reality.

However, different crushing and/or grinding methods, for a crystal structure, can lead to difference in the cleavage and fracture. Feng [6] compared the effects of dry and wet grinding on the flotation of complex sulphide ores from the Merensky Reef in South Africa. The dry ground samples had relatively rough particle surfaces with a high concentration of microstructural defects, exhibiting more stable, higher loaded froths and faster flotation

* Corresponding author.
E-mail address: csuwangyh@163.com (Y. Wang).

http://dx.doi.org/10.1016/j.apsusc.2015.08.257
0169-4332/

kinetics, owing to the activated particle surfaces, while the wet ground samples with smoother, cleaner surfaces presented higher concentrate grades and slightly higher recoveries. Some investigators also studied the influences of shape and morphological properties of particles ground by different grinding methods on such subsequent processes as flotation [7–12]. They drew the conclusion that particles ground by different grinding methods had various shapes and there was a correlation between the surface properties, such as flatness, roundness, relative width, elongation ratio and hydrophobicity of particles.

It is well known that spodumene is an anisotropic mineral with very prominent cleavage at {1 1 0} plane [13]. In the crystal model of spodumene, the chains of silicate tetrahedron $[SiO_3]^{2-}$ are bound together laterally through the ionic bonding with Li^+ and Al^{3+} in octahedral coordination. Aluminum is in octahedral coordination with six oxygens, including two non-bridging basal oxygens and four apical oxygens. Lithium in spodumene coordinates with six oxygens consisting of two non-bridging basal oxygens, two bridging basal oxygens and two apical oxygens [5,14,15].

Considering the anisotropic characteristic of spodumene and the fact that grinding method can affect the cleavage and fracture of minerals, experiments of wet and dry grinding of spodumene were carried out, and the effect of grinding methods on the cleavage of spodumene as well as on their flotation behavior were discussed in this study. Properties of several cleavage planes of spodumene were studied.

2. Experimental procedure

2.1. Materials and reagents

Single spodumene bulks, obtained from Keketuohai Rare Metal Mine (Altay district, Xinjiang, China), were crushed by hammer and picked by hand. Then the handpicked high-purity spodumene was crushed by a corundum jaw crusher to −3 mm and finally the removal of iron impurities using dry strong magnetic separator was carried out to eliminate iron contamination. The chemical composition of the samples is shown in Table 1.

The grinding tests were operated in a laboratory porcelain mill at 30 rpm. The grinding media were agate balls with different diameters, including 10 mm, 15 mm, 20 mm and 25 mm. 500 g of spodumene samples were placed in the porcelain mill and ground for 5 min each run. The experiments of wet and dry grinding were guaranteed performing under the same conditions except that the wet grinding used 250 mL deionized water. After a run, the wet and dry ground products were passed through a standard screen with a pore size of 105 μm (150 mesh), respectively. The oversize products returned the mill for the next run. The process was repeated until sufficient amount of samples in size fraction of −105 μm were obtained for the following experiments.

Subsequently, the two kinds of ground spodumene samples were screened to get different size ranges, including −105 + 38 μm, −105 + 75 μm, −75 + 45 μm, −45 + 38 μm and −38 + 23 μm, respectively. All the samples were rinsed with deionized water and dried at temperature of 60 °C.

Sodium oleate of analytical quality was used as the collector in the micro-flotation tests. Solutions of HCl and NaOH were applied for pH adjustment of the system. The standard of deionized water is: electrical resistivity > 18.2 MΩ (25 °C), TOC (total organic carbon) < 10 ppb, DO (dissolved oxygen) < 10 ppb, number of −0.05 μm particle < 200/L; no bacteria.

Table 1
Chemical composition of spodumene samples (%).

Li_2O	Al_2O_3	SiO_2	Fe_2O_3	Na_2O	K_2O	CaO	MnO	P_2O_5	BeO	Ta_2O_5	Nb_2O_5
7.81	25.99	62.74	0.54	0.312	0.156	0.36	0.127	0.16	0.028	0.019	0.028

2.2. Micro-flotation tests

Micro-flotation tests were performed in a laboratory flotation apparatus at 1700 rpm. Both wet and dry ground spodumene samples in different size ranges were used as the feed. 2 g of the samples and appropriate amount of deionized water were placed in a 20 mL plexiglas cell for each test. 6×10^{-4} mol/L sodium oleate was added after the adjustment of the pulp pH by HCl and NaOH solutions, and the pulp was then conditioned for 2 min. The froth product was collected for a total time of 3 min. All the flotation tests were carried out at room temperature of around 25 °C. In the end, the concentrates and tailings were filtered, dried, and weighed to calculate the flotation recovery of spodumene.

2.3. X-ray diffraction (XRD) measurements

The XRD measurements were performed on a DX-2700 diffractometer with CuKα radiation (at 40 kV, 40 mA) under a step width of 0.02° and a counting time of 0.02 s/step. The ground samples of spodumene were prepared without any further grinding. Using a side-packed holder and tapping the holder gently to consolidate the powder to make sure that the samples were randomly oriented [16]. The XRD data were analyzed using the Jade 6.5 program.

2.4. Scanning electron microscope (SEM)

Scanning electron microscopy of JSM-6490LV model was used for the measurement of morphology. Samples were stuck on the mode with double sided carbon tape, and coated with Pt to make them conducting.

2.5. Specific surface area (BET) measurements

BET (Brunauer–Emmett–Teller) measurements were carried out on a Quantachrome SI gas adsorption analyzer to determine the specific surface area of the two kinds of ground spodumene with size fraction of −105 + 38 μm. The specific surface area was determined using a 6-point method with nitrogen as adsorption gas. Three independent BET measurements were carried out under a constant condition, and the average value of experimental data was adopted as the final result.

2.6. Adsorption of sodium oleate on ground samples

The adsorption of sodium oleate on both wet and dry ground samples in size fraction of −105 + 38 μm was studied under various solution pH conditions. After the addition of reagents and the stirring of pulp, the suspensions were feed into a plastic tube to be centrifuged at 9000 rpm for 15 min. Finally, the supernatant was taken and placed in a glass tube for the adsorption density measurement on a Shimadzu TOC-L analyzer using conventional combustion catalytic oxidation method. Three independent measurements were carried out under a constant condition, and the average value of experimental data was adopted as the final result. The adsorption density of sodium oleate was then calculated by the following equation:

$$\Gamma = \frac{(C_0 - C) \times V}{1000 \times M \times 2 \times S} \quad (1)$$

where Γ is the amount (mol/m^2) of collector adsorbed on mineral surface, C_0 and C are the concentrations (mg/L) of the initial collector solution and the collector-equilibrated solution respectively. V